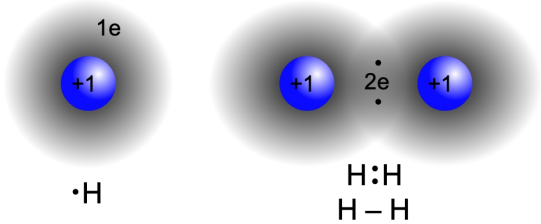
Dr. Michelle Ernst | 08.03.2023

Intermolecular covalent interactions

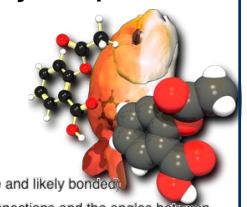
- The notion of covalency dates back to the very early days of quantum chemistry:

> **„we shall denote by the term “covalence” the number of pairs of electrons which a given atom shares with its neighbors“ (Langmuir, 1919)**

- It is an equally crucial but also fuzzy concept in chemistry.



- The transition between covalent bond and non-covalent interactions is **continuous**.
- This carries over to the transition between inter- and intramolecular.
- Chemical visualization software draw bonds based solely on pre-defined interatomic distances.



Bonds in GaussView Cont.

When no connectivity info present, GV infers bonding:
- Determined from GV table of atomic pair distances
- Used for the Clean function
- Customizable via GV Preferences (*Expert feature!*)

Elem. 1	Elem. 2	Triple	Double	Resonant	Single	Weak
C	C	1.2474	1.386	1.4476	1.6324	0
N	C	1.1907	1.323	1.3818	1.5582	0

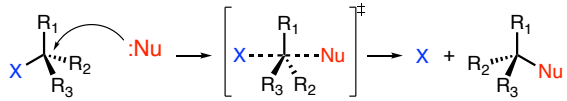
Expected bonds appear to be “missing” in unusual structures
- Use distance+chemical intuition to determine whether bond interaction exists

gaussian.com

Loosely speaking, the steps are something like this:
- Determine atomic connection (from atoms which are close and likely bonded)
- Determine atom type/hybridization from the number of connections and the angles between them (e.g., sp, sp2, sp3)
- Run a quick "aliasing" check -- to have a double or triple bond, the atom must have at least one neighbor which could also have a double or triple bond.
- Check for possibly aromatic rings (i.e., 5 and 6-member rings which are close to planar)
- Run an aromaticity check on these possibly aromatic rings and assign Kekule bonds
- Run a check for typical functional groups with multiple bonds
- Last, but not least, fill any remaining multiple bond valences. For example, in a carbon which could have two possible double bonds, pick the neighbor which has the shortest bond distance.

Examples of continuous change from covalent to non-covalent bonds

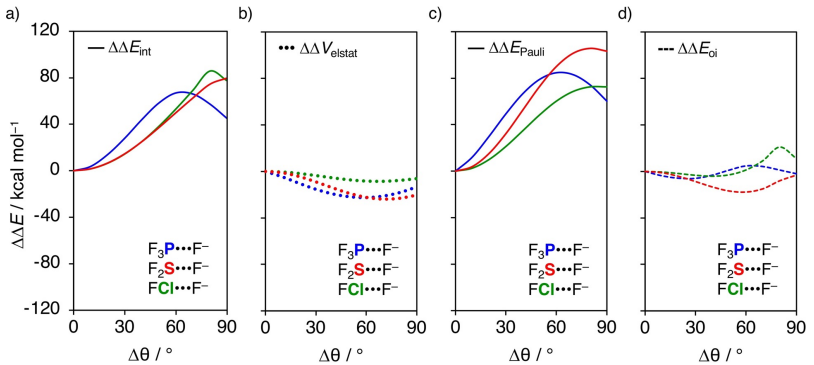
S_N2 reaction:



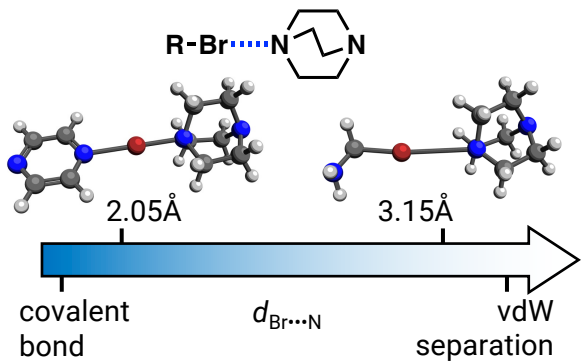
Hydrogen shift in oxalic acid with increasing pressure:

Formation of intermolecular pnictogen, chalcogen, and halogen bonds due to covalent contributions

Chem. Eur. J. **2022**, e202203791.

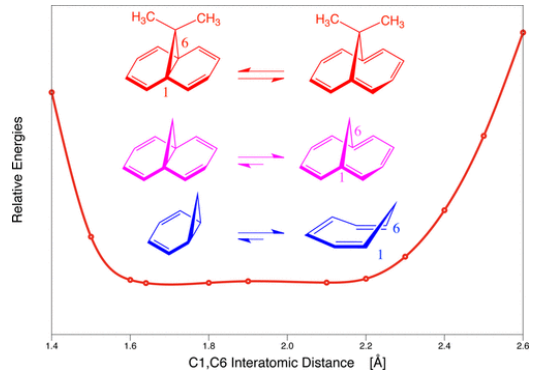


Complexes between DABCO and R-Br electrophiles: changing from 1.946 Å in $F_5Pyr\text{-}Br^+$ to 3.154 Å in $CH_2Br(NH_2)$



Chem. Commun. **2018**, *54*, 8060.

C-C distance in bridged annulenes:



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